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Keimpe Jan Van Den Berg et al.

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For: PHOTOACTIVATIBLE WATER BORNE
COATING COMPOSITION

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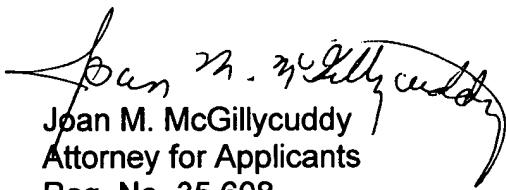
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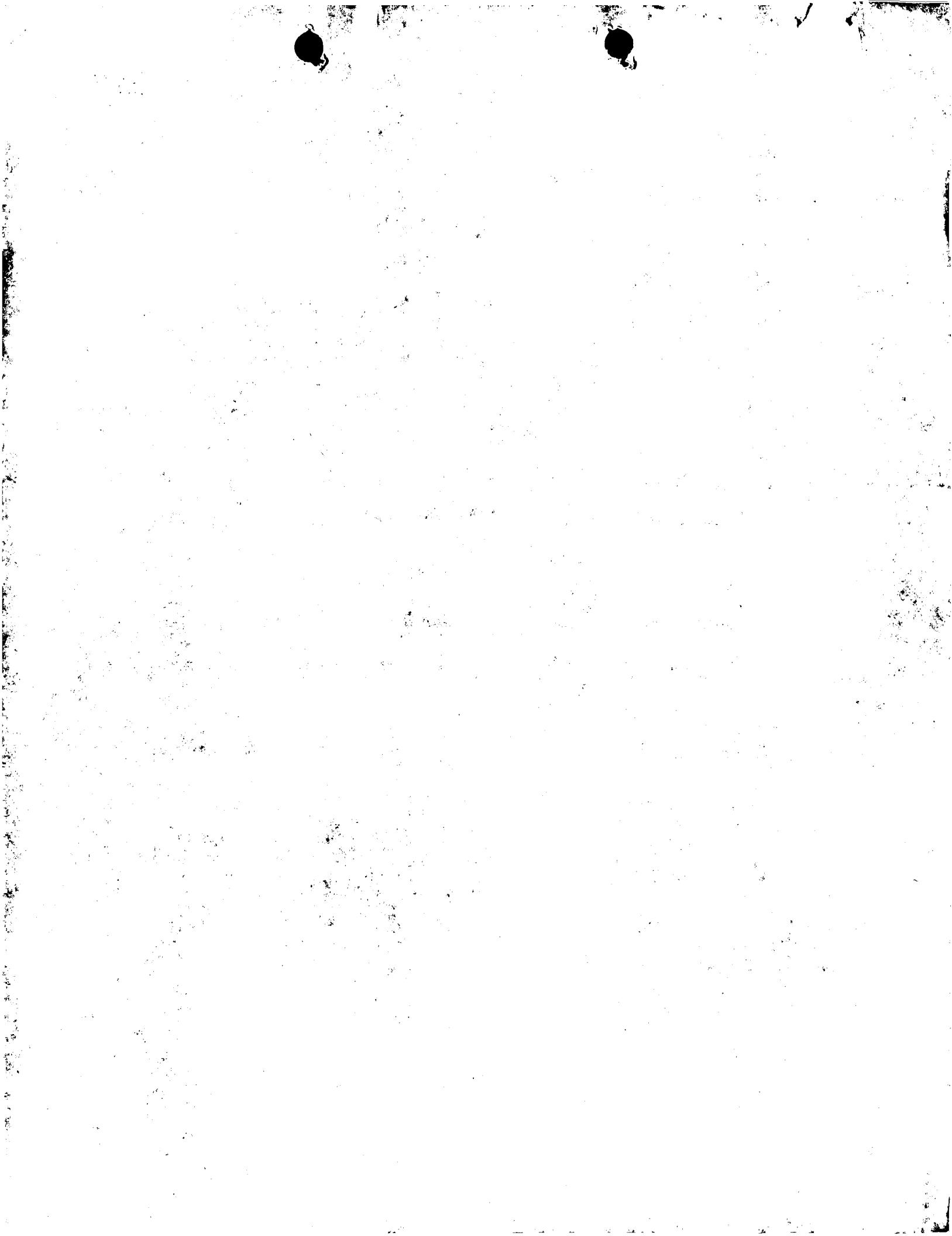
Sir:

Enclosed herewith is a certified copy of European Patent Application No. 00203722.4 filed October 25, 2000 in connection with the above-identified application.

Respectfully submitted,


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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00203722.4

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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ACO 2833 PDEP

PHOTOACTIVATABLE WATER BORNE COATING COMPOSITION

The invention relates to a photoactivatable water borne coating composition comprising a (meth)acryloyl-functional polyurethane dispersion and a UV-
5 initiator.

Photoactivatable coating compositions of the type indicated above are known from, int. al., EP-A-0 952 170. The system disclosed therein is based on dual cure and therefore comprises, besides a (meth)acryloyl-functional polyurethane dispersion, free isocyanate groups which may further react with one or more active hydrogen atoms in the aqueous coating composition. Though high-quality coating layers can be obtained with the known water borne coating compositions, the properties of the aqueous polyurethane dispersions used in the known compositions are still a subject for improvement, especially as far as 10 the appearance of layers containing said dispersions is concerned when applied over substrates with rough surfaces.
15

Photoactivatable polyurethane dispersions as such for use in clear coats were already known from DE-C-196 35 447. In this document use is made of a 20 polyurethane- and/or polyester-(meth)acrylate binder with diacrylate monomers as reactive diluents. While the compositions are said to be suitable for use in solvent borne and water borne compositions, in the examples solvent borne compositions only are employed, which are cured by pulsed high-energy ultraviolet radiation.

EP-A-0 965 621 discloses a photoactivatable coating composition which 25 comprises a (meth)acryloyl-functional polyurethane and a photoinitiator such as phenylglyoxylic acids or their esters or salts or derivatives thereof, optionally with other photoinitiators. Though explicit mention is made of the possible use 30 of the claimed coating compositions in water borne systems, in the examples only solvent borne systems are used.

ACO 2833 PDEP

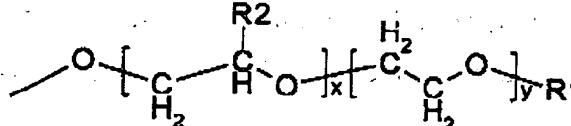
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The invention now provides water borne coating compositions which do not detract from the performance when applied over substrates with rough surfaces and which need not be cured by pulsed high-energy ultraviolet radiation, but can be cured with UV light such as UV-A light. Furthermore, it has been found

5 that the resins used in the water borne coating compositions of the present invention cannot be used as such in a solvent borne coating composition, especially when the solvent borne coating composition is used as a clearcoat over basecoat.

10 The invention consists in that the (meth)acryloyl-functional polyurethane of the known type mentioned in the opening paragraph comprises 5 to 25 wt.% of alkylene oxide groups.

15 The preferred alkylene oxide groups in the (meth)acryloyl-functional polyurethane are ethylene oxide groups, but alternatively propylene oxide groups or mixtures of ethylene oxide and propylene oxide groups are useful as well. For example, the alkylene oxide groups may be C₁-C₄ alkoxy ethers of polyalkylene glycols with the structure:

20 

wherein R1 is a hydrocarbon radical with 1 to 4, preferably 1 or 2, carbon atoms; R2 is a methyl group; x is between 0 and 40, preferably between 0 and 20, most preferably between 0 and 10; y is between 0 and 50, and x+y is between 2 and 50, preferably between 2 and 25. Examples are the methoxy ethers of polyethylene glycols or polypropylene glycols having a number average molecular weight between 500 and 3,000, preferably between 200 and 1,500, most preferably between 350 and 1,000.

ACO 2833 PDEP

3

Thus far very good results have been obtained with a (meth)acryloyl-functional polyurethane comprising 8 to 18 wt.% of alkylene oxide groups.

Superior results are generally obtained with a (meth)acryloyl-functional polyurethane wherein the number average molecular weight of the (meth)acryloyl-functional polyurethane is in the range of 1,000 to 20,000, whereas optimum results have been obtained with a (meth)acryloyl-functional polyurethane having a number average molecular weight in the range of 1,200 to 8,000.

10 A special feature of the water borne coating compositions according to the invention is their good appearance as a clear coat when applied over a (metallic) base coat. Said good appearance as a result of optimum cross-link density and shrinkage of the obtained film is shown to full advantage when the

15 equivalent weight of the (meth)acryloyl-functional polyurethane dispersion is in the range of 200 to 3,333 on solid, preferably between 350 to 1000.

The (meth)acryloyl groups-containing polyurethane dispersions can be prepared using conventional methods of polyurethane synthesis by conversion 20 of polyisocyanates with hydroxyalkyl (meth)acrylates and a chain extender if desired. Suitable chain extenders include diols, polyols, dithiols, polythiols, diamines, and polyamines.

Preference is given to a (meth)acryloyl-functional polyurethane which is 25 obtainable by reaction of:

- a) at least one organic polyisocyanate,
- b) optionally, at least one organic compound containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000,
- c) at least one isocyanate-reactive and/or diisocyanate compound bearing non-ionic dispersing groups,
- d) at least one isocyanate-reactive (meth)acryloyl-functional compound,

ACO 2833 PDEP

4

- e) optionally, at least one active hydrogen-containing chain extender, and
- f) optionally, at least one active hydrogen-containing compound bearing ionic groups.

5. The organic polyisocyanate (a) used in making the (meth)acryloyl-functional polyurethane polymer may be an aliphatic, cycloaliphatic or aromatic di-, tri- or tetra-isocyanate that may be ethylenically unsaturated or not, such as 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 10 2,2,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, ω,ω' -dipropylether diisocyanate; 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate, dicyclohexyl methane-4,4'-diisocyanate (Desmodur® W), toluene diisocyanate, 15 1,3-bis(isocyanatomethyl) benzene, xylylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl xylylene diisocyanate (TMXDI®), 1,5-dimethyl-2,4-bis(2-isocyanatoethyl) benzene, 1,5-dimethyl-2,4-bis(2-isocyanatoethyl) benzene, 1,3,5-triethyl-2,4-bis(isocyanatomethyl) benzene, 4,4'-diisocyanato-diphenyl, 3,3'-dichloro-4,4'-diisocyanato-diphenyl, 3,3'-diphenyl-4,4'-diisocyanato-20 diphenyl, 3,3'-dimethoxy-4,4'-diisocyanato-diphenyl, 4,4'-diisocyanato-diphenyl methane, 3,3'-dimethyl-4,4'-diisocyanato-diphenylmethane, diisocyanato-naphthalene, the adduct of 2 molecules of a diisocyanate, for example hexamethylene diisocyanate or isophorone diisocyanate, to a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate to 1 molecule of water (available under the trademark Desmodur N of Bayer), the adduct of 1 molecule of trimethylol propane to 3 molecules of toluene diisocyanate (available under the trademark Desmodur L of Bayer), the adduct of 1 molecule of trimethylol propane to 3 molecules of isophorone diisocyanate, compounds such as 1,3,5-triisocyanatobenzene and 2,4,6-triisocyanatotoluene, 25 and the adduct of 1 molecule of pentaerythritol to 4 molecules of toluene diisocyanate.

dilisocyanate. It is preferred that use be made of an aliphatic or cycloaliphatic di- or trisocyanate containing 8-36 carbon atoms.

Mixtures of polyisocyanates can be used and also polyisocyanates which have
5 been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

The organic compounds (b) containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000
10 which may be used in the preparation of the (meth)acryloyl-functional polyurethane preferably are polymeric organic polyols terminated by hydroxyl groups. The organic polyols particularly include diols and triols and mixtures thereof but higher-functionality polyols may be used, for example as minor components in admixture with diols. The polyols may be selected from the
15 group of polyesters, polyester amides, polyethers, polythioethers, polycarbonates, polyacetals, polyolefins, and polysiloxanes. Preference is given to polyols having a molecular weight in the range of 700 to 3,000.

Polyester polyols which may be used include hydroxyl-terminated reaction
20 products of polyhydric alcohols, such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, furan dimethanol, dimethylol cyclohexane, glycerol, trimethylol propane or pentaerythritol or mixtures thereof with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic,
25 glutaric, and adipic acids, or their dimethyl esters, phthalic anhydride, hexahydrophthalic anhydride or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a polyol, may also be used.

30 Polyester amides may be obtained by the inclusion of aminoalcohols such as ethanol amine in the polyesterification mixtures.

Suitable polyether polyols include polyalkylene oxide glycol wherein alkylene oxide may be selected from ethylene oxide and/or propylene oxide units.

Polythioether polyols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, dicarboxylic acids, formaldehyde, aminoalcohols or aminocarboxylic acids.

Polycarbonate polyols include products obtained by reacting diols, such as 1,3-propane diol, 1,4-butane diol, 1,6-hexane diol, 1,4-cyclohexane dimethanol, diethylene glycol or tetraethylene glycol, with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers.

In order to ensure that the (meth)acryloyl-functional polyurethane is self-dispersible in water, at least one isocyanate-reactive and/or diisocyanate compound bearing non-ionic groups (c) is included as reactant in the preparation of the (meth)acryloyl-functional polyurethane.

Suitable non-ionic dispersing groups are the mono C₁-C₄ alkoxy derivatives disclosed above. Preferably, the (meth)acryloyl-functional polyurethane comprises 8 to 18 wt.% of alkylene oxide groups. Suitable C₁-C₄ polyalkylene oxide compounds contain at least one hydroxyl group. Examples are methoxy polyethylene oxide glycols, methoxy polyethylene oxide-1,3-diols such as Tegomer® D-3123 (PO/EO = 15/85; Mn = 1,180), Tegomer® D-3409 (PO/EO = 0/100; Mn = 2,240), and Tegomer® D-3403 (PO/EO = 0/100; Mn = 1,180) available from Goldschmidt AG, Germany. Optimum results are obtained with a (meth)acryloyl-functional polyurethane wherein the polyalkylene oxide units are polyethylene oxide units.

ACO 2833 PDEP

7

The mono C₁-C₄ alkoxy derivatives may be used as such or incorporated into an adduct. For example, the adduct of a polycarboxylic acid, a polyol, and one of the above-mentioned C₁-C₄ alkoxy derivatives may be used. Examples of polycarboxylic acids include dicarboxylic acids or their ester-forming derivatives,

5 for example succinic, glutaric, and adipic acids, or their dimethyl esters, phthalic anhydride, hexahydrophthalic anhydride or dimethyl terephthalate, or mixtures thereof. Examples of the polyol include ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, furan dimethanol, dimethylol cyclohexane, glycerol, di(trimethylolpropane), trimethylol

10 propane or pentaerythritol or mixtures thereof.

As isocyanate-reactive (meth)acryloyl-functional compounds (d) may be used hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, and polypropylene glycol mono-(meth)acrylate.

Superior results are generally obtained with the addition products of difunctional or polyfunctional epoxy compounds and (meth)acrylic acid. As examples of suitable difunctional or polyfunctional epoxy compounds, which as such may be 20 solid or liquid, may be mentioned the diglycidyl or polyglycidyl ethers of (cyclo)aliphatic or aromatic hydroxyl compounds, such as ethylene glycol, glycerol, cyclohexane diol, and mononuclear or polynuclear difunctional or trifunctional phenols and bisphenols such as bisphenol-A and bisphenol-F; epoxidised aliphatic and/or cycloaliphatic alkenes, such as dipentene dioxide, 25 dicyclopentadiene dioxide, and vinyl cyclohexene dioxide. Thus far good results have been obtained with difunctional epoxides selected from the group of hydrogenated bisphenol-A diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, and neopentylglycol diglycidyl ether.

30 As active hydrogen-containing chain extenders (e), compounds bearing groups which are reactive with isocyanate groups can be used. The chain extender may be water, but also an organic polyol, a polyamine or a polythiol.

ACO 2833 PDEP

8

Preferably, organic polyols include compounds having a weight average molecular weight of less than 400. These include diols and triols and mixtures thereof, but higher-functionality polyols may also be used. Examples of such lower-molecular weight polyols include ethylene glycol, diethylene glycol, 5 tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, furan dimethanol, glycerol, trimethylol propane, and the reaction products up to molecular weight 400 of such polyols with propylene oxide and/or ethylene oxide.

10 Optionally, at least one isocyanate-reactive and/or diisocyanate compound bearing ionic groups (f) may be included as reactant in the preparation of the (meth)acryloyl-functional polyurethane. Examples include dimethylol propionic acid, sulfosuccinate diol, fosfonate diol, mono hydroxy acids (hydroxy-carboxylic acids), hydroxy sulfonic acids, hydroxy fosfonic acid and all possible salts of 15 these acids.

More preferably, the (meth)acryloyl-functional polyurethane is obtainable by reaction of:

a) at least one organic polyisocyanate,

20 b) at least one isocyanate-reactive and/or diisocyanate compound bearing non-ionic dispersing groups,

c) at least one isocyanate-reactive (meth)acryloyl-functional compound, and

d) at least one active hydrogen-containing chain extender,
or

25 e) by reaction of

f) at least one organic polyisocyanate,

g) at least one isocyanate-reactive and/or diisocyanate compound bearing non-ionic dispersing groups,

h) at least one isocyanate-reactive (meth)acryloyl-functional compound, and

i) at least one active hydrogen-containing compound bearing ionic groups.

ACO 2833 PDEP

9

The (meth)acryloyl-functional polyurethane suitable for preparing the water borne coating compositions according to the invention may be prepared in a conventional manner by reacting a stoichiometric amount or an excess of the organic polyisocyanate (a) with the other reactants (c) and (d) and, optionally, 5 (b), (e), and (f) under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until the reaction between the isocyanate groups and the isocyanate-reactive groups is substantially complete. The reactants are generally used in proportions corresponding to a ratio of 10 isocyanate groups to isocyanate-reactive (usually hydroxyl) groups of from about 1:1 to about 6:1, preferably about 1:1. If an excess of the organic polyisocyanate (a) is used, an isocyanate-terminated prepolymer is prepared in a first step. In a second step, at least one isocyanate-reactive group containing compound such as chain extender (e) can be added. The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient 15 temperatures are from about 5°C to 95°C or, more preferably, from about 10°C to about 45°C.

Polyurethanes which incorporate (meth)acryloyl functionality preferably contain a proportion of (meth)acryloyl groups in the polymer within the range of 30 to 20 500 milli-equivalents, preferably 60 to 250 milli-equivalents, per 100 g of polyurethane polymer.

Preferably, the coating composition of the present invention comprises one or more reactive diluents. Compounds suitable as reactive diluents generally are 25 ethylenically unsaturated compounds. As representative examples of such may be mentioned those compounds disclosed in the previously incorporated EP-A-0 965 621. The reactive diluent preferably has a molecular weight of from about 80 to about 800, more preferably about 100 to about 400. Compounds meeting the molecular weight requirement are suitable for lowering the viscosity of the 30 coating composition. Preferably, reactive diluents are used in an amount of 5 to 50 wt.% on solid resin, more preferably 10 to 40 wt.%.

Examples of monofunctional reactive diluents include the esters of acrylic and methacrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tertiary butyl (meth)acrylate, neopentyl (meth)acrylate, isopentyl (meth)acrylate, n-hexyl (meth)acrylate, isoheptyl (meth)acrylate, n-heptyl (meth)acrylate, iso-heptyl (meth)acrylate, octyl (meth)acrylate, iso-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, iso-nonyl (meth)acrylate, decyl (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, iso-undecyl (meth)acrylate, dodecyl (meth)acrylate, iso-dodecyl (meth)acrylate, tridecyl (meth)acrylate, iso-tridecyl (meth)acrylate, tetradecyl (meth)acrylate, iso-tetradecyl (meth)acrylate, and mixtures thereof. Moreover, the aforesaid esters of acrylic and methacrylic acid may contain radiation-reactive unsaturation in the alcohol radical as well. Additional monofunctional radiation-sensitive compounds which may be used as a reactive diluent include diallyl maleate, diallyl fumarate, vinyl acetate, and N-vinyl-2-pyrrolidone, especially the last compound.

The highly preferred reactive diluents in the clear coats of the present invention are those having more than one radiation-sensitive bond. Such compounds ordinarily are the esters of acrylic or methacrylic acid and a polyhydric alcohol. Further suitable reactive diluents are urethane acrylates, melamine acrylates, epoxy-acrylic acid adducts, and reactive diluents containing polyethylene oxide. Examples of the aforesaid difunctional diluents are ethylene glycol diacrylate and dimethacrylate; isopropylene and propylene glycol diacrylate and dimethacrylate. Similarly, the diol diacrylates and dimethacrylates of butane, pentane, hexane, heptane, and so forth up to and including thirty-six carbon diols are useful in the present clear coats as reactive diluents. Of particular interest are 1,4-butane diol diacrylate, 1,6-hexane diol diacrylate, diethylene glycol diacrylate, trimethylol propane triacrylate, and pentaerythritol tetraacrylate. Thus far optimum results have been obtained with reactive diluents selected from the group of 3-methoxypropyl-, benzyl-, octyl-, 2-hydroxy-ethyl citraconimide, (meth)acrylate esters of butane diol, hexane diol, and

ACO 2833 PDEP

11

trimethylolpropane, the diacrylate ester of butanediol diglycidyl ether, ethoxylated trimethylol propane triacrylate, and the reaction product of $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl xylylene diisocyanate (TMXDI[®]) with 4-hydroxy butylacrylate and/or the esterification product of 1 mole of 2-hydroxyethyl acrylate and 2 moles of 5 caprolactone, and/or methoxy polyethyleneoxide glycol having a molecular weight between 300 and 1,000.

As examples of UV-initiators which can be used in the clear coats of the invention may be mentioned benzoin ether (Esacure[®] ex Fratelli Lamberti), 10 benzyl dimethyl ketone acetal (Irgacure[®] 651 ex Ciba), 1-hydroxy cyclohexyl phenyl ketone (Irgacure[®] 184 ex Ciba), 2-hydroxy-2-methyl-1-phenyl propane-1-one (Darocur[®] 1173 ex Ciba), 1-(4-isopropyl phenyl)-2-hydroxy-2-methyl propane-1-one (Darocur[®] 1116 ex Ciba), diethoxyacetophenone (DEAP[®] ex Upjohn), methyl thioxanthone (Quantacur[®] ex Shell), 2,4,6-trimethylbenzoyl 15 diphenyl phosphine oxide (Lucirin TPO[®] ex BASF), and the bisphosphine oxides such as CGI[®] 819 and CGI[®] 403 ex Ciba. The amount of UV-initiator used ranges from 0.001 to 10 wt.% on solids, preferably from 1 to 8 wt.%, more preferably from 2 to 6 wt.%.

20 The coating compositions according to the invention are radiation curable after application and, optionally, evaporation of solvents. In particular, they are suitable for curing by irradiation with UV radiation. Combinations of IR/UV irradiation are also suitable. Radiation sources which may be used are those customary for UV, such as high- and medium-pressure mercury lamps.

25 In order to avoid any risk involved in handling UV light of very short wave length (UV B and/or UV C light), preference is given, especially for use in automotive refinishing shops, to fluorescent lamps, which produce the less injurious UV A light.

30

The amount of energy necessary to cure the reactive components will of course depend on the light intensity, the angle of exposure to and distance from the radiation, and the thickness of the coating to be applied, as well as the presence or absence of a free radical initiating catalyst. For any given 5 composition the best method of determining the amount and duration of the radiation required is by experimental determination of the amount of radiation-sensitive groups not cured following exposure to the radiation source is.

In circumstances where it appears to be desirable to increase the curing speed 10 in places which are not readily accessible to UV light, the water borne coating composition may comprise one or more active hydrogen atoms-containing groups which can react with the ethylenically unsaturated groups contained in the (meth)acryloyl-functional polyurethane dispersion. Suitable active hydrogen-containing groups are activated CH group-containing compounds containing a 15 methylene and/or monosubstituted methylene group in the α -position to two carbonyl groups, such as malonate and/or acetoacetate group-containing compounds. Examples of malonate group-containing compounds and malonate group-containing oligomeric and polymeric compounds are disclosed in US-A-2,759,913 and US-A-4,602,061, respectively. Preferred compounds are the 20 oligomeric and/or polymeric malonate group-containing compounds such as polyurethanes, polyesters, polyacrylates, epoxy resins, polyamides; and polyvinyl resins which contain malonate groups in the main chain or are pendant or both.

25 Malonate group-containing polyurethanes can be obtained, for example, by reacting a polyisocyanate with a hydroxyl group-containing ester of a polyol and malonic acid, or by the esterification or transesterification of a hydroxy-functional polyurethane with malonic acid or a dialkylmalonate.

30 Malonate group-containing polyesters can be obtained, for example, by the polycondensation of malonic acid, an alkyl malonic acid (such as ethyl malonic acid), a mono- or dialkyl ester of such a malonic acid and/or the reaction

product of a malonic ester and an alkyl (meth)acrylate, optionally with other di- or polycarboxylic acids, with di- and/or higher-functional hydroxy compounds, and, optionally, monofunctional hydroxy and/or carboxyl compounds.

- 5 Malonate group-containing epoxy esters can be obtained, for example, by esterifying an epoxy resin with malonic acid or a malonic monoester, or by transesterification with a dialkyl malonate, optionally with other carboxylic acids and derivatives thereof.
- 10 Malonate group-containing polyamides can be obtained, for example, in the same manner as the polyesters, in which case at least part of the hydroxy compound is replaced with a mono- and/or polyvalent primary and/or secondary amine.
- 15 As examples of acetoacetate group-containing compounds may be mentioned acetoacetic esters as disclosed in US-A-2,759,913 (see especially col. 8, lines 53-54), diacetoacetate compounds as disclosed in US-A-4,217,396 (see especially col. 2, line 65 through col. 3, line 27), and acetoacetate group-containing oligomeric and polymeric compounds as disclosed in US-A-20 4,408,018 (see especially col. 1, line 51 through col. 2, line 6). Preference is given to the oligomeric and/or polymeric acetoacetate group-containing compounds.

Suitable acetoacetate group-containing oligomeric and polymeric compounds can be obtained, for example, from polyalcohols and/or hydroxy-functional polyether, polyester, polyacrylate, vinyl and epoxy oligomers and polymers by reaction with diketene or transesterification with an alkyl acetoacetate. Such compounds can also be obtained by the copolymerisation of an acetoacetate-functional acrylic monomer with other vinyl- and/or acrylic-functional monomers.

30

Especially preferred among the acetoacetate group-containing compounds for use with the present invention are acetoacetate group-containing oligomers and

polymers containing at least 2 acetoacetate groups. It is also especially preferred that such acetoacetate group-containing compounds have an Mn in the range of from about 234 to about 30,000, and an acid number of about 2 or less.

5

Compounds containing both malonate and acetoacetate groups in the same molecule are also suitable and can be obtained, for example, by a Michael reaction between a malonate-functional polyester and an acetoacetate-functional acrylic compound (e.g., acetoacetoxyethyl acrylate). Additionally, physical mixtures of malonate and acetoacetate group-containing compounds are suitable. Alkylacetoacetates can, in addition, be used as reactive diluents.

10

Optionally, the activated CH groups-containing compounds may be utilised in the enamine form, such as disclosed in EP-A-0 420 133.

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The reaction between CH-acid compounds and olefinically unsaturated compounds is carried out in the presence of a base. It is preferred that use be made of a base of which the conjugated acid has a pKa of at least 12, such as tetrabutyl ammonium hydroxide, epoxy adduct of tertiary amines, amines of the amidine type, examples of which include tetramethyl guanidine and 1,8-diaza-[5,4,0]-bicycloundecene, and catalysts described in EP-A-0 596 461. Thus far, optimum results have been obtained with 1,8-diaza-[5,4,0]-bicycloundecene.

25

According to the invention, electrically charged bases also constitute suitable catalysts, provided that the conjugated acid thereof has a pKa > 10, preferably > 12. As examples of representative bases may be mentioned metal bases. Examples of suitable bases include metal oxides such as sodium methanolate; metal hydroxides such as sodium phenolate; metal hydrocarbon compounds such as n-butyl lithium; metal hydrides such as sodium hydride; metal amides such as potassium amide, and metal carbonates such as potassium carbonate.

Instead of CH-acid compounds the composition may comprise polyamines such as polyamino amides having an amine number of 60-1,000, which react with the (meth)acrylate groups present in the (meth)acryloyl-functional polyurethane dispersion, such as disclosed in EP-A-0 262 720. Use may also be made of 5 oligomeric sterically hindered polyamines, such as disclosed in EP-A-0 678 105.

Preference is given to a coating composition which comprises compounds having active hydrogen atoms-containing groups such as hydroxyl-, thiol-, and/or amino-functional groups which are reactive with free isocyanate groups.

10 For use in the water borne coating compositions according to the invention preference is given to compounds bearing hydroxyl-functional groups. If desired, the hydroxyl groups may be comprised in the (meth)acryloyl-functional polyurethane dispersion.

15 For an organic polyisocyanate to be used in a water borne dual cure coating composition preference is given to a hydrophobic polyisocyanate including polyfunctional, preferably free, polyisocyanates with an average NCO functionality of 2.5 to 5 which may be (cyclo)aliphatic, araliphatic or aromatic in nature. The polyisocyanate may include biuret, urethane, uretdione, and 20 isocyanurate derivatives. One example of a polyisocyanate includes 1,6-hexane diisocyanate, isophorone diisocyanate or bis(isocyanate cyclohexyl) methane, and the above-mentioned derivatives thereof. Normally, these products are liquid at ambient temperature and commercially available in a wide range. Preferred are cyclic trimers (isocyanurates) of 1,6-hexane diisocyanate and 25 isophorone diisocyanate. Usually these compounds contain small quantities of their higher homologues. Optionally, a hydrophilic polyisocyanate may be partially substituted for the hydrophobic polyisocyanate. The polyisocyanate, the (meth)acryloyl-functional polyurethane dispersion, and, optionally, a further hydroxyl-functional compound or resin should be mixed in such a ratio that the 30 NCO:OH ratio is in the range of 0.5-3:1, preferably 0.75-2.5:1, and more preferably 1-2:1.

The polyisocyanate may be mixed into the (meth)acryloyl-functional polyurethane dispersion by any suitable technique. However, simple stirring is usually sufficient. Sometimes it may be useful to dilute the polyisocyanate somewhat with an organic solvent like ethyl acetate or 1-methoxy-2-propyl acetate to reduce its viscosity. Also included in the free isocyanate groups-containing coating compositions may be reactive diluents such as water-soluble mono or (preferably) polyhydric alcohols, examples of which include ethylene glycol, propylene glycol, isomeric butane diols, the polyethylene oxide glycols or polypropylene oxide glycols, trimethylol propane, pentaerythritol, and glycerol.

In the presence of a free polyisocyanate generally use is made of a Sn-based catalyst. The pot life at ambient temperature of a free polyisocyanate composition generally is between 4 and 12 hours, depending on the use of the catalysts and their amount.

The coating compositions may further comprise other ingredients, additives or auxiliaries, such as other polymers or polymer dispersions, pigments, dyes, emulsifiers (surfactants), pigment dispersion aids, levelling agents, anti-cratering agents, antifoaming agents, antisagging agents, heat stabilisers, UV absorbers, antioxidants, and fillers.

Suitable types of other polymer dispersions include acrylic polymer emulsions and aqueous polyurethane dispersions.

The coating compositions of the present invention may be applied to any substrate. The substrate may be, for example, metal, plastic, such as PVC, wood, glass, ceramic material, or some other coating layer. The other coating layer may be comprised of the coating composition of the invention or it may be a different coating composition. The coating compositions of the invention show particular utility as clear coats, base coats, pigmented top coats, primers, and fillers. The coating compositions can be applied by conventional means such as by spray gun, brush, or roller, with spraying being preferred. Curing

ACO 2833 PDEP

17

temperatures preferably are between 0 and 80°C and more preferably between 20 and 60°C. The compositions are particularly suitable in the preparation of coated metal substrates, such as in the refinish industry, in particular the body shop, to repair automobiles and transportation vehicles, and in finishing large
5 transportation vehicles such as trains, trucks, buses, and aeroplanes.

Preferred is the use of the coating composition of the present invention as a clear coat. Clear coats are required to be highly transparent and must adhere well to the base coat layer. It is further required that the clear coat does not
10 change the aesthetic aspect of the base coat by strike-in, i.e. discolouration of the base coat due to its solvation by the clear coat composition, or by yellowing of the clear coat upon outdoor exposure. A clear coat based on the coating composition of the present invention does not have these drawbacks.

15 In the case of the coating composition being a clear coat, the base coat may be a conventional base coat known in the coating art. Examples are solvent borne base coats, e.g., Autobase® ex Sikkens, and water borne base coats, e.g., Autowave® ex Sikkens. Furthermore, the base coat may comprise pigments (coloured pigments, metallics and/or pearls), wax, solvents, flow additives,
20 neutralising agent, and defoamers. Also high-solids base coats can be used. The clear coat composition is applied to the surface of a base coat and then cured. An intermediate curing step for the base coat may be introduced.

25 In another preferred embodiment the coating composition of the present invention may be applied as a clearcoat on flexible flooring, such as PVC and polyolefin. Preferred application method is then the use of a roller coater.

30 The invention will be illustrated with reference to the following examples. Of course these examples are submitted for a better understanding of the invention only; they are not to be construed as limiting in any manner the scope thereof.

Examples**Methods**

5 The dispersions' respective average particle size was determined with the aid of dynamic light scattering, with the dispersions diluted to a solids content of about 0.1 wt.%.

The solids content was determined in accordance with ASTM method No. 1644-
10 59, with heating to 140°C over a period of 30 minutes.

The weight average molecular weight Mw and the number average molecular weight Mn were determined using gel permeation chromatography with polystyrene as the standard.

15 The Persoz Hardness of the obtained coating layers was determined after 1 and 7 days of ageing in accordance with French industrial standard method NF T30-016, the result being expressed in seconds.

20 The resistance to methylethyl ketone (MEK) and water was determined after 1 and 7 days of ageing and exposure for one minute (MEK) or for one hour (water). In the resistance test 0 stands for dissolved, 3 for slightly affected, and 5 for excellent.

25 The appearance was judged visually. A good appearance means: a smooth surface with a high gloss. A bad appearance means: a dull, low gloss level.

The scratch resistance was judged by pressing and scratching a finger-nail on the coating. (-) means: the coating is damaged very easily; (+) means: severe pressure is necessary to damage the coating.

The adhesion evaluation was done with the cross cut test. For the wet adhesion test, the samples were left in water for 5 days and then dried for 1 hour. The rating ranges from 0 to 5 where 5 is the best.

5 Preparation of acryloyl-functional polyurethane dispersion A

a) *Preparation of a polyester comprising polyethylene oxide groups*

A 3 l 4-neck flask fitted with a variable speed stirrer, thermocouples in combination with a controller, a distillation column, a reflux condenser, a nitrogen sparge, and a heating mantle was charged with a mixture composed of

10 332 g of hexahydrophthalic anhydride and 1,614 g of polyethylene glycol monomethyl ether of an average molecular weight of 750. The mixture was heated to 170°C for 30 minutes, cooled to 140°C, and 269 g of di(trimethylol-propane) were added, followed by 132 g of xylene and 3.3 g of a 85% aqueous phosphoric acid solution. The mixture was heated to 235°C, and water was
15 azeotropically distilled off until the acid value of the reaction mixture was below 5 mg KOH/g. The mixture was then cooled to 180°C, and xylene was distilled off at reduced pressure. The resulting polyester diol solidified at room temperature and had an acid value of 3.9 mg KOH/g and a hydroxyl value of 59 mg KOH/g.

20

b) *Preparation of an acryloyl-functional diol*

A 2-litre 4-neck flask, which was fitted with a variable speed stirrer, a thermo-couple, a dry air sparge via the head space, a dip tube, and a heating mantle was charged with 573 g of hydrogenated bisphenol-A-diglycidyl ether

25 (Eponex® 1510 ex Shell), 17.5 g of acrylic acid, and 0.56 g of 2,6-ditert. butyl p-cresol. The mixture was heated to 95°C while bubbling with dry air. A mixture of 157.7 g of acrylic acid, 0.56 g of 2,6-ditert. butyl p-cresol, and 0.75 g of chromium 2-ethylhexanoate was added dropwise in approximately 3 hours. The temperature of the reaction mixture was maintained between 95 and 100°C.

30 Stirring at this temperature was continued until the acid value of the reaction

mixture had dropped below 5 mg KOH/g. The prepared adduct was cooled and diluted with 97 g of dry 2-butanone.

5 *c) Preparation of an acryloyl-functional polyurethane dispersion comprising polyethylene oxide groups*

A 3 l 4-neck flask fitted with a variable speed stirrer, thermocouples in combination with a controller, a condenser, a dry air sparge, and a heating mantle was charged with a mixture composed of 273.2 g of acryloyl-functional diol b), 146.7 g of polyester a), 12.26 g of trimethylol propane, 99.1 g of 4-hydroxybutyl acrylate, 260.8 g of Desmodur® W (a polyisocyanate ex Bayer), 1.50 g of 2,6-ditert. butyl-p-cresol, and 250 g of 2-butanone. The mixture was heated to 45°C and stirred until homogeneous, while bubbling with dry air. Then 0.94 g of tin(II) octanoate was added after one hour of stirring. The reaction mixture was stirred for approximately six hours at 80°C until the isocyanate content was < 0.1 wt.%. Then, 3 ml of ethanol 100% was added, and stirring was continued for about 30 minutes. The reaction mixture was cooled to 45°C. After dilution of the reaction mixture with 154 g of 2-butanone the stirrer speed was increased, and 1,125 g of water were added at a rate of 12 ml/min. After all the water had been added, a distillation head and a vacuum pump were connected to the flask and the pressure was gradually lowered until all 2-butanone was distilled off. A white emulsion with the following characteristics was obtained: solids content 44%, equivalent weight 535 on solids, Mn 2,686, Mw 11,153, pH 5.5, and particle size 120 nm.

25 *Preparation of an acryloyl-functional polyurethane dispersion comprising ammonium carboxylate and polyethylene oxide groups B*

A 3 l 4-neck flask fitted with a variable speed stirrer, thermocouples in combination with a controller, a condenser, a dry air sparge, and a heating mantle was charged with a mixture composed of 264.3 g of Desmodur® W, 300 g of dry 2-butanone, and 0.87 g of tin(II) octanoate. The mixture was heated to 70°C while bubbling with dry air. Then a pre-mixed homogeneous mixture of

45°C consisting of 273.6 g of acryloyl-functional diol b), 52.8 g of polyester a), 16.7 g of dimethylol propionic acid, 108.5 g of 4-hydroxybutyl acrylate, 1.40 g of 2,6-ditert. butyl-p-cresol, and 270 g of 2-butanone was added dropwise in such a way that the exothermic reaction was kept at 80°C. The reaction was
5 continued while stirring for about 6 hours at 80°C. A further portion of 0.87 g of tin(II) octanoate was added after one hour of stirring. The reaction mixture was stirred for approximately six hours at 80°C until the isocyanate content was < 0.1 wt.%. Then 3 ml of ethanol 100% was added, and stirring was continued for about 30 minutes. The reaction mixture was cooled to 45°C. Subsequently, 95%
10 of the acid groups of the reaction mixture was neutralised with N,N-dimethyl ethanolamine. The stirrer speed was increased, and 1,125 g of water were added at a rate of 12 ml/min. After all the water had been added, a distillation head and a vacuum pump were connected to the flask and the pressure was gradually lowered until all 2-butanone was distilled off. A white emulsion with
15 the following characteristics was obtained: solids content 47%, equivalent weight 560 on solids, Mn 2,286, Mw 6,476, pH 8.8, and particle size 120 nm.

Preparation of an acryloyl-functional polyurethane dispersion comprising sulfo groups and polyethylene oxide groups C

20 a) *Preparation of a sulfosuccinate diol*

To a 5-litre, four-neck round-bottomed flask fitted with a condenser, a thermocouple, a stirrer, and a nitrogen inlet were added 1,249.5 g of Cardura E10 ex Shell Chemicals. The temperature was raised to 140°C, and then 290.3 g of maleic acid were added in portions in one hour. Thereafter the reaction
25 mixture was heated with stirring at 150°C. After reaching an acid number lower than 2 mg KOH/g, the reaction temperature was lowered to 95°C. Then 475 g of water, 710 g of Dowanol-PM ex Dow Chemicals, and 228.0 g of sodium dithionite were added, and stirring was continued for one hour at 60°C and for another hour at 95°C. Water and Dowanol were then distilled off from the
30 reaction mixture at reduced pressure while the last traces were distilled off azeotropically with 300 g of o-xylene. The reaction mixture was then cooled

down to room temperature, 600 g of dry 2-butanone were added, and the precipitate was filtered off from the product.

b) Preparation of an acryloyl-functional polyurethane dispersion comprising

5 sulfo groups and polyethylene oxide groups

To a 2-litre, four-neck round-bottomed flask fitted with a condenser, a thermocouple, a stirrer, and a dry air inlet reaching within the reaction mixture were added 144.7 g of Desmodur® W, 0.43 g of tin(II)octanoate, and 70 g of dry 2-butanone. This solution was heated and at 70°C over one hour a mixture of 10 166.0 g of acryloyl-functional diol b), 39.1 g of polyester a), 62.7 g of sulfo-succinate diol a), 63.3 g of 4-hydroxybutylacrylate, 0.8 g of ionol, and 70 g of dry 2-butanone was added. Thereafter another 0.43 g of tin(II)octanoate was added, and the reaction mixture was heated with stirring at 80°C until the isocyanate content was < 0.1 wt.%. Then the remaining isocyanate was 15 quenched with ethanol.

250 g of this solution were added to 266 g of water in 1.5 hours at 50°C with vigorous stirring. Stirring was continued for 1.5 hours at 50°C, and then 2-butanone was removed from the dispersion by distillation under reduced pressure. A dispersion with the following characteristics was obtained: solids 20 content 44.4%, equivalent weight 506 on solids, Mn 1,781, Mw 5,231, pH 6.9, and particle size 229 nm.

Preparation of an acryloyl-functional polyurethane dispersion comprising sulfo groups and polyethylene oxide groups D

25 To a 2-litre, four-neck round-bottomed flask fitted with a condenser, a thermocouple, a stirrer, and a dry air inlet reaching within the reaction mixture were added 120.9 g of Desmodur® W, 0.28 g of tin(II)octanoate, and 60 g of dry 2-butanone. This solution was heated and at 70°C over one hour a mixture of 30 131.6 g of acryloyl-functional diol b), 44.4 g of polyester a), 39.8 g of sulfosuccinate diol a), 53.5 g of 4-hydroxybutylacrylate, 0.5 g of ionol and 60 g of dry 2-butanone was added. Thereafter another 0.20 g of tin(II)octanoate was

added, and the reaction mixture was heated with stirring at 80°C until the isocyanate content was < 0.1 wt.%. Then the remaining isocyanate was quenched with ethanol. 410 g of this product were added to 395 g of water in 1.5 hours at 50°C with vigorous stirring. Stirring was continued for 1.5 hours at 5 50°C, and then 2-butanone was removed from the dispersion by distillation under reduced pressure. A dispersion with the following characteristics was obtained: solids content 43.2%, equivalent weight 458 on solids, Mn 1,934, Mw 6,687, and particle size 207 nm.

10 Preparation of an acryloyl-functional polyurethane dispersion comprising sulfo groups and polyethylene oxide groups E

To a 2-litre, four-neck round-bottomed flask fitted with a condenser, a thermocouple, a stirrer, and a dry air inlet reaching within the reaction mixture were added 116.8 g of Desmodur® W, 0.27 g of tin(II)octanoate, and 60 g of dry 15 2-butanone. This solution was heated and at 70°C over one hour a mixture of 144.4 g of acryloyl-functional diol b), 62.7 g of polyester a), 9.7 g of sulfosuccinate diol a), 50.3 g of 4-hydroxybutylacrylate, 0.85 g of ionol, and 60 g of dry 2-butanone was added. Thereafter another 0.41 g of tin(II)octanoate was added, and the reaction mixture was heated with stirring at 80°C until the 20 isocyanate content < 0.1 wt.%. Then the remaining isocyanate was quenched with ethanol.

235 g of this product were added to 244 g of water in 1.5 hours at 50°C with vigorous stirring. Stirring was continued for 1.5 hours at 50°C, and then 2-butanone was removed from the dispersion by distillation under reduced 25 pressure. A dispersion with the following characteristics was obtained: solids content 49.4%, equivalent weight 449 on solids, Mn 2,071, Mw 7,663, and particle size 837 nm.

Examples 1 to 5

The following coating compositions were prepared.

Coating composition 1 contained 50.0 g of acryloyl-functional polyurethane dispersion A (solids content 24.3 g), to which were added 7.50 g of water, 2.50 g of butylglycol, 0.25 g of BYK 346 (wetting agent with a solids content of 0.12 g), and 1.28 g of Darocur® 1173 (UV-initiator ex Ciba).

Coating composition 2 equaled composition 1, except that 7.30 g of Craynor 132 (an acryloyl-functional reactive diluent ex Cray Valley) had been added.

Coating composition 3 contained 50.0 g of acryloyl-functional polyurethane dispersion B (solids content 20.0 g), to which were added 2.50 g of butylglycol, 0.25 g of BYK 333 (wetting agent with a solids content of 98%), and 0.83 g of Lucirin TPO-L (UV-initiator ex BASF).

Coating composition 4 equaled composition 3 after the addition of 6.23 g of Craynor 132.

Coating composition 5 contained 50.0 g of acryloyl-functional polyurethane dispersion A (solids content 25.15 g), to which were added 7.50 g of water, 2.50 g of butylglycol, 0.25 g of BYK 333, 7.55 g of Craynor 132, and 1.31 g of Lucirin TPO-L.

Compositions 1-4 were applied on tin plated panels by draw-bar (100 µm wet application thickness). Compositions 1-5 were applied on a blue metallic water borne base coat (Autowave®) by spraying. All clearcoats had a dry layer thickness in the range of 65 to 90 µm. The panels were dried until all the water had evaporated (at least 90 minutes at room temperature or 30 minutes at 60°C). The films were subsequently irradiated for 10 minutes at room temperature with sun tanning lamps (TL 09, distance 10 cm).

The properties of the obtained coating layers on tin plated panels (in the case of compositions 1 to 4) or on a water borne base coat (in the case of composition

5 for all properties and of compositions 1-4 for appearance determination) are given in Table 1.

Table 1

Example	Persoz Hardness		Resistance to MEK		Resistance to water		Appearance and scratch resistance	Layer thickness (μm)
	1 day	7 days	1 day	7 days	1 day	7 days		
1	167	238	3-4	3-4	5	5	Moderate/ +	67
2	165	181	5	5	5	5	Good/ +	71
3	157	170	3-4 ¹⁾	3-4 ¹⁾	3-4 ²⁾	3-4 ²⁾	Poor/ -	80
4	133	120	3-4 ¹⁾	3-4 ¹⁾	3-4 ²⁾	3-4 ²⁾	Poor/ -	79
5	n.d.	n.d.	3-4	3-4	5	5	Good/ +	86

¹⁾ Top-layer of the film dissolved

5 ²⁾ Film became hazy after 1 hour's exposure to water

The appearance of the coating layers obtained with compositions 2 and 5 was the best. These experiments show that coating compositions comprising (meth)acryloyl-functional polyurethane having 8 to 18 wt.% alkylene oxide groups are preferred. Even more preferred are these coating compositions comprising a reactive diluent.

Comparative Example A

Prepared was a solvent borne coating composition A containing 50.0 g of a solution of an acryloyl-functional polyurethane (as described for dispersion A) in methylethyl ketone with Craynor 132 (solids content 44.7 g) as reactive diluent and, further, 1.00 g of butylglycol, 21.43 g of butyl acetate, 16.07 g of methylethyl ketone, and 1.88 g of Darocur[®] 1173.

20 After application on a blue metallic water borne base coat (Autowave[®]) by spraying, the obtained coating layer was dried and irradiated in a manner analogous to that disclosed for the layers obtained with Examples 1 to 5. The properties of the coating layer obtained with the solvent borne coating composition detracted from the performance. The coating layer was highly coloured.

Examples 6 to 8

Each coating composition 6 to 8 contained 50.0 g of acryloyl-functional polyurethane dispersion A (solids content 24.3 g), to which had been added 7.50 g of water, 2.50 g of butylglycol, 0.25 g of BYK 346 (wetting agent with a 5 solids content of 0.12 g), and 1.28 g of Darocur[®] 1173. The respective compositions further comprised 10 wt.% (based on the polyurethane dispersion) of Sartomer[®] 214 (1,4-butanediol dimethacrylate ex Sartomer) (composition 6), 10 wt.% (based on the polyurethane dispersion) of Sartomer[®] 239 (1,6-hexanediol dimethacrylate ex Sartomer) (composition 7), and 30 wt.% (based 10 on the polyurethane dispersion) of Sartomer[®] 350 (trimethylol propane trimethacrylate ex Sartomer) (composition 8).

After application on a tin plate the obtained coating layers were dried and irradiated in a manner analogous to that disclosed for the layers obtained with 15 Examples 1 to 5. The properties of the cured coating layers on tin plated panels (with compositions 6 to 8) are given in the Table below.

Table 2

Example	Pereoz Hardness		Resistance to MEK		Resistance to water		Appearance and scratch resistance	Layer thickness (μm)
	1 day	7 days	1 day	7 days	1 day	7 days		
6	210	209	3-4	3-4	5	4	Good	72
7	226	217	3-4	3-4	5	4	Good	75
8	235	239	3-4	3-4	5	4	Good	78

20 Coating compositions 6, 7, and 8 were also applied on a blue metallic water borne base coat (Autowave[®]). All three coatings had a good appearance.

Examples 9 to 12

Four acryloyl-functional polyurethane dispersions with different amounts of 25 alkylene oxide groups were tested in the following coating compositions (amounts are given in grams):

	9	10	11	12
Dispersion A	20.0	-	-	-
Dispersion E	-	20.0	-	-
Dispersion D	-	-	20.0	-
Dispersion C	-	-	-	20.0
Water	5.0	3.0	3.0	3.0
Butyl glycol	1.0	1.0	1.0	1.0
Byk 346	0.1	0.1	0.1	0.1
Darocur 1173	0.47	0.51	0.45	0.46
Craynor 132	2.70	2.96	2.59	2.66

The formulations were applied on tin plates and on a blue metallic water borne base coat (Autowave®). Drying and curing was performed as described in Examples 1 to 5. The results are outlined in the following table.

5

Formulation	Layer thickness (μm)	Resistance to MEK (1 day ageing)	Resistance to water (1 day ageing)	Percoz hardness (s) after 1 day ageing	Appearance over base coat	Scratch resistance
9	79	5	5	185	good	+
10	90	4	5	188	good	+
11	75	3-4	5	197	good	+/-
12	77	3-4	3-4	199	good	-

These experiments show also that coating compositions comprising (meth)acryloyl-functional polyurethane having 8 to 18 wt.% alkylene oxide groups and a reactive diluent are preferred.

10

Example 13

The following formulation was tested (amounts are given in grams):

Dispersion A	20,0
Water	3,0
Butyl glycol	1,0
BYK 346	0,1
3-methoxypropylcitraconimide	2,92
Darocur 1173	0,51

5 This formulation was applied on a tin plate and on a blue metallic water borne base coat (Autowave®). Drying and curing was carried out as described for Examples 1-5.

The film had the following characteristics:

10

Example	Persoz Hardness		Resistance to MEK		Resistance to water		Appearance and scratch resistance	Layer thickness (µm)
	1 day	7 days	1 day	7 days	1 day	7 days		
13	171	175	4	4	5	5	good/ +	74

Example 14 and comparative example B

The following coating compositions were prepared (amounts are given in grams):

5

		14	B
Lux 101 VP	Aliphatic polyurethane dispersion (s.c. 40%) ex Alberdingk Boley	34.8	87
Dispersion B		52.2	—
Esacure KIP 100F	Photoinitiator ex Lamberti	1.3	1.3
Speedcure BEM	Photoinitiator ex Lambson	0.4	0.4
Byk 346	Defoamer ex Byk Chemie	0.3	0.3
Byk 333	Levelling agent ex Byk Chemie	0.2	0.2
Orgasol 2001	Polyamide wax ex Elf Atochem	10.5	10.5
Borshigel LW44	Polyurethane thickner	0.3	0.3

The formulations were applied on PVC flooring by roller coater, between 10 to 50 g/m². The coated substrates were dried until all the water had evaporated (3 minutes at 120°C). The films were subsequently irradiated at a belt speed of 5

10 to 10 minutes per minute with a 80 W/cm mercury lamp. The results are outlined in the following table.

Formulation	Dry adhesion	Wet adhesion
14	5	5
B	3	0

Other properties such as chemical resistance and flexibility are on the same

15 level or better than the comparative example.

Example 15 and comparative example C

The following coating compositions were prepared (amounts are given in grams):

5

		15	C
Lux 101 VP	Aliphatic polyurethane dispersion (s.c. 40%) ex Alberdingk Boley	20.6	31.7
Dispersion B		32.5	----
Primal E-3120	Acrylic emulsion (s.c. 40%) ex Rohm & Haas	39.6	61.0
Esacure KIP 100F	Photoinitiator ex Lamberti	1.5	1.5
Speedcure BEM	Photoinitiator ex Lambson	0.5	0.5
Dehydran 1293	Defoamer ex Cognis	0.6	0.6
Byk 346	Defoamer ex Byk Chemie	0.3	0.3
Byk 333	Levelling agent ex Byk Chemie	0.2	0.2
Orgasol 2001	Polyamide wax ex Elf Atochem	3.8	3.8
Acrysol RM-2020	Polyurethane thickner ex Rohm & Haas	0.4	0.4

The formulations were applied on polyolefin flooring by roller coater, between 10 to 50 g/m². Drying and curing was carried out as described for example 14. The results are outlined in the following table.

10

Formulation	Dry adhesion	Wet adhesion
15	5	5
C	3	0

Other properties such as chemical resistance and flexibility are on the same level or better than the comparative example.

ACO 2833 PDEP

31

Claims

1. Photoactivatable water borne coating composition comprising a (meth)acryloyl-functional polyurethane dispersion and a UV-initiator, characterised in that the (meth)acryloyl-functional polyurethane comprises 5 to 25 wt.% of alkylene oxide groups.
2. Water borne coating composition according to claim 1, characterised in that the (meth)acryloyl-functional polyurethane comprises 8 to 18 wt.% of alkylene oxide groups.
3. Water borne coating composition according to any one of the preceding claims, characterised in that the coating composition comprises a reactive diluent.
4. Water borne coating composition according to any one of the preceding claims, characterised in that the number average molecular weight of the (meth)acryloyl-functional polyurethane is in the range of 1,200 to 8,000.
5. Water borne coating composition according to any one of the preceding claims, characterised in that the proportion of (meth)acryloyl groups in the polymer is within the range of 3 to 500 milli-equivalents per 100 g of polyurethane polymer.
6. Water borne coating composition according to any one of the preceding claims, characterised in that the (meth)acryloyl-functional polyurethane is obtainable by reaction of:
 - a) at least one organic polyisocyanate,
 - b) optionally, at least one organic compound containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000,

ACO 2833 PDEP

32

- c) at least one isocyanate-reactive and/or diisocyanate compound bearing non-ionic dispersing groups,
- d) at least one isocyanate-reactive (meth)acryloyl-functional compound,
- e) optionally, at least one active hydrogen-containing chain extender, and
- f) optionally, at least one active hydrogen-containing compound bearing ionic groups.

7. Water borne coating composition according to any one of the preceding claims, characterised in that the (meth)acryloyl-functional polyurethane comprises isocyanate-reactive groups such as hydroxyl groups and the dispersion further comprises an organic polyisocyanate.

8. Water borne coating composition according to claim 7, characterised in that the equivalent ratio of the isocyanate-reactive groups in the (meth)acryloyl-functional polyurethane to the free isocyanate groups in the dispersion is between 0.5:2.0 and 2.0:0.5.

9. Water borne coating composition according to any one of the preceding claims, characterised in that the coating composition is a water borne clear coat.

10. Method of coating a substrate which comprises applying a water borne coating composition according to any one of the preceding claims to a substrate, causing or allowing the aqueous based carrier phase of the composition to be removed, and curing the surface of the film obtained with UV light.

11. Method of coating a substrate which comprises applying a water borne coating composition according to either of preceding claims 7 and 8 to a substrate, causing or allowing the aqueous based carrier phase of the composition to be removed, curing the surface of the film obtained with UV

ACO 2833 PDEP

33

light, and allowing the unexposed layers to cure thoroughly at room temperature or with heating.

12. Method of coating a metal substrate with a base coat composition and a clearcoat composition, characterised in that the clearcoat comprises a (meth)acryloyl-functional polyurethane dispersion having 8 to 18 wt.% of alkylene oxide groups, a reactive diluent, and a UV-initiator.
13. Method of coating a flexible flooring with a clearcoat composition, characterised in that the clearcoat composition comprises a (meth)acryloyl-functional polyurethane dispersion having 5 to 25 wt.% of alkylene oxide groups, a reactive diluent, and a UV-initiator.

ACO 2833 PDEP

34

14. ABSTRACT

Photoactivatable water borne coating composition comprising a (meth)acryloyl-functional polyurethane dispersion and a UV-initiator, wherein the (meth)acryloyl-functional polyurethane comprises 5 to 25 wt.% of alkylene oxide groups. Preferably, the (meth)acryloyl-functional polyurethane comprises 8 to 18 wt.% of alkylene oxide groups. More preferably, the coating composition comprises a reactive diluent.

The (meth)acryloyl-functional polyurethane is obtainable by reaction of:

- 10 a) at least one organic polyisocyanate,
- b) optionally, at least one organic compound containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 8,000,
- c) at least one isocyanate-reactive and/or diisocyanate compound bearing non-
15 ionic dispersing groups,
- d) at least one isocyanate-reactive (meth)acryloyl-functional compound,
- e) optionally, at least one active hydrogen-containing chain extender, and
- f) optionally, at least one active hydrogen-containing compound bearing ionic
groups.

20 The water borne coating composition is especially suitable for application as a clear coat.